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(71)Applicant : KUMAMOTO SEIFUN KK
(72)Inventor : IMAMURA MASAHIRO
TOKUMITSU KIYONORI
OKAZAKI KENJI
HONDA OSAMU

(54) PRODUCTION OF VITAMIN K SUPPLEMENT COMPOSITION FOR FOOD AND METHOD FOR EXTRACTING VITAMIN K

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a process for producing a vitamin K supplement compsn. for food having a high vitamin K content without the occurrence of problems in safety and palatability in spite of addition of this vitamin to the food by a relatively simple processing method using natural materials as raw materials and a method for extracting the vitamin K having no possibility of remaining and forming (denaturation) of harmful materials.
SOLUTION: The leaf parts of dark green and yellow vegetables having green leaf blade parts are used as the materials to be treated and are heated to soften the plant tissues and, thereafter, the leaf parts are subjected to a solid liquid sepn. of liquid mesophyll parts, solid petile parts and veinparts, thereby the compsn. consisting of the mesophyll parts and having the high vitamin K content is obtd. According to another method for production, the dry matter of the leaf parts is pulverized and the pulverized matter is classified to the mesophyll parts, the petiole parts and the vein parts to separate the dry matter of the mesophyll parts. The vitamin K content of the resulted compsn. is ≥1000μm per 100g. The selective extraction of the vitamin K is made possible if the dark green and yellow vegetables are extracted by using liquid carbon dioxide existing in a supercritical state.

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CLAIMS

[Claim(s)]
[Claim 1] The manufacture approach of the food-grade vitamin K supply constituent characterized by carrying out solid liquid separation to the liquefied mesophyll section, a solid leaf pedicel, and the vein section, and separating the solid of the mesophyll section with a high vitamin K content from the obtained liquefied mesophyll section after [in the deep yellow vegetables which have the green leaf blade section] heating a leaf at least and softening the plant tissue.
[Claim 2] The manufacture approach of the food-grade vitamin K supply constituent characterized by the thing in the deep yellow vegetables which have the green leaf blade section for which the dry matter of a leaf is ground at least, the grinding object is classified in the mesophyll section, a leaf pedicel, and the vein section, and the dry matter of the mesophyll section with a high vitamin K content is separated.
[Claim 3] The manufacture approach of a food-grade vitamin K supply constituent that the vitamin K content of the mesophyll section separated by the approach according to claim 1 or 2 is more than 1000microper 100g g.
[Claim 4] The extract approach of the vitamin K characterized by carrying out extract processing of the deep yellow vegetables which have the green leaf blade section using the carbon dioxide in a supercritical condition which liquefied.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the manufacture approach of the food-grade vitamin K supply constituent which consists of the mesophyll section which contains the vitamin K contained in deep yellow vegetables in high concentration, and the extract approach of a vitamin K. It can add to for example, pans, noodles, confectionary, a drink, etc., and the above-mentioned vitamin K supply constituent can be used as a gestalt of food. Moreover, a vitamin K can be used as drugs besides food.
[0002]
[Description of the Prior Art] As for a vitamin K, in liver, it is required for generation of the prong thrombin which is an important factor related to blood coagulation, and the deficiency disease has the lack nature intracranial hemorrhage in a newborn infant and a suckling, and there is among the breast feeding children by two months after the birth especially in a suckling. [many] Although people can use the vitamin K generated with enterobacilli, since there is no production of a vitamin K into the intestines of a newborn infant and a suckling, it is supposed that it will be easy to suffer from a deficiency disease. Therefore, vitamin K addition modified milk powder is also marketed so that a vitamin K can be supplied by direct breast feeding for a newborn infant and a suckling. On the other hand, it is taking in a natural vitamin K from everyday food to a parent, and it is desirable to raise the vitamin K content in mother's milk. by the advance of the iatrotechnique in recent years, and fullness of social welfare, Japan is becoming a rapid aging society compared with a foreign country, and abnormalities are caused to a bony metabolic turnover as a social problem in it — osteoporosis — there is a disease. In the osseous tissue, as a result of repeating the osteogenesis by the osteoclasis by the osteoclast, and osteoblast, this balance's collapsing in aging, a menopause, etc. and osteoclasis's exceeding osteogenesis, **** decreases and it is thought that it results in osteoporosis. Moreover, in connection with the lack of energy intake of a diet of the younger age group in recent years etc., there is lack of calcium intake and we will be anxious about low age-ization of osteoporosis in the future.
[0003] Although the current cure to these diseases has the calcium preparations which control osteoclasis, vitamin D, estrogen, parathyroid hormone, calcitonin, etc., the cure which promotes osteogenesis is not known despite former. By research in recent years, it becomes clear that osteogenesis is promoted because a vitamin K uses together with calcium, and the importance of a vitamin K came to be recognized further. The vitamin K is comparatively contained in vegetable oil, cobwebbing fermented soybeans, deep yellow vegetables, seaweed, etc. at high concentration. However, it is difficult to take in such food in large quantities at once, and cooking above-mentioned specific food every day will force the burden on eating habits upon a lactating woman, an old man, an after [a menopause] woman, etc., and it is not desirable on nutrition balance.
[0004]
[Problem(s) to be Solved by the Invention] In order to supply a vitamin K to food, it is desirable to add a natural material with a high vitamin K content, and the vitamin K extract technique in the deordorization distillate now generated at the purification process of vegetable oil and vegetable oil is known. As a technique of extracting the vitamin K in vegetable oil, there are approaches, such as the i column-chromatography method, ii distillation, and iii solvent fractionation, conventionally.
i) The approach the column-chromatography method uses organic solvents, such as alcohol, an acetone, and n-hexane, for a mobile phase, using silica gel, the silica gel which carried out chemical modification as a stationary phase is learned. By the column-chromatography method, since the target matter can be separated and refined quite correctly, the enrichment factor of a natural vitamin K is high, but in order to maintain a stationary phase and a mobile phase, great costs are needed.
ii) Distillation is performed by the simple distillation mold which a molecule moves to a concentration side from an evaporation side in an one direction, and is called vacuum distillation or molecular distillation. Although molecular distillation can be condensed comparatively cheaply compared with the column-chromatography method, faults, such as reduction of the natural vitamin K in an elevated temperature with a low enrichment factor and fear of a residual of an organic solvent, are mentioned.
iii) After dissolving the method of solvent fractionation dissolving vegetable oil or a deordorization distillate with the low-grade monohydric alcohol of carbon numbers 1-4 etc., and cooling and depositing an impurity, or the above-mentioned deordorization distillate in low-grade monohydric alcohol, a natural vitamin K is made to stick to activated carbon, and the approach of separating and refining is learned for the low polar solvent which is the aliphatic series or aromatic hydrocarbon of carbon numbers 5-10. As compared with two above-mentioned approaches, although this solvent fractionation can be condensed cheaply, its enrichment factor is low. And in order to extract using organic solvents, such as a harmful methanol and n-hexane, great heat energy is needed from an extract for removal and recovery of a solvent. Moreover, it is not only apprehensive about decomposition of the natural vitamin K by heat, but like the above-mentioned distillation ii, in order that the problem of the residual of an extract solvent may remain, a complicated separation process and severe quality control are needed.
[0005] Although the vitamin K is stable with heat compared with other vitamins, there is a property which is easy to be decomposed with light, oxygen, and alkali. In vegetable oil and a deordorization distillate, the above-mentioned deordorization distillate also has the fault with it that it is the natural material which is easy to oxidize, including polyunsaturated fatty acid mostly. As a material of other natural vitamin Ks, since there is a peculiar fermentation smell and the upper viscosity matter is

contained so much, cobwebbing fermented soybeans are not desirable from the field of palatability and workability. Although deep yellow vegetables are so much satisfactory from the field of palatability and workability, ** is comparatively large, and the problem is left behind to abundant intake while [of a content] it has been a green leaf. Moreover, if organic solvents, such as an acetone, n-hexane, and ethanol, tend to extract the vitamin K contained in the leaf of deep yellow vegetables at abundance, the gum-like matter will generate and removing an organic solvent completely will reach to an extreme of difficulty. Furthermore, when monohydric alcohol is used as an extract solvent, there is a problem that a part of chlorophyll which is coloring matter contained in a leaf denaturalizes to harmful matter called a pheophorbide. Then, the purpose of this invention is to offer [to cancel an above-mentioned trouble, about a natural material, for there to be no problem in safety or palatability, even if it adds for food by the comparatively easy processing approach as a raw material, and] the manufacture approach of a food-grade vitamin K supply constituent with a high vitamin K content. Moreover, another purpose of this invention is to offer the extract approach of a vitamin K without fear of the residual of the harmful matter, and generation (denaturation).

[0006]

[The means for solving invention] The place to which research was wholeheartedly come in piles about the simple method of processing a natural material this invention persons were suitable for vitamin K strengthening to food, Also in the above-mentioned natural vitamin K material, the difference of the mesophyll section of the plant tissue and other organs on the strength is used paying attention to the deep yellow vegetables with which a vitamin K is chiefly contained in the mesophyll section. By separating the mesophyll section which contains many vitamin E, beta-carotene, etc. other than a vitamin K, by extracting a vitamin K from deep yellow vegetables by using a liquefaction carbon dioxide as an extract solvent again, it finds out that said purpose can be attained and came to complete this invention. Namely, the manufacture approach of the food-grade vitamin K supply constituent of this invention A leaf is heated at least. it can set to the deep yellow vegetables which have the green leaf blade section -- After softening the plant tissue, solid liquid separation is carried out to the liquefied mesophyll section, a solid leaf pedicel, and the vein section. It is characterized by separating the solid of the mesophyll section with a high vitamin K content from the obtained liquefied mesophyll section, or grinding the dry matter of the above-mentioned leaf, classifying the grinding object in the mesophyll section, a leaf pedicel, and the vein section, and separating the dry matter of the mesophyll section. Moreover, the extract approach of the vitamin K of this invention is characterized by carrying out extract processing of the deep yellow vegetables which have the green leaf blade section using the carbon dioxide in a supercritical condition which liquefied.

[0007]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. as the deep yellow vegetables which have the green leaf blade section in this invention -- a chive and tomorrow -- a leaf, the Osaka Chinese cabbage, a barilla plant, white radish sprouts, and a mustard seed -- a vegetable, Potherb mustard, Chinese cabbage, ****, and a shantung -- a vegetable, a perilla, and garland chrysanthemum -- immediately -- ****, Japanese parsley, Chinese mustard, boy choy, a New Zealand spinach, a vine purple, shepherd's purse, a scallion, nozawana, parsley and Hino -- a vegetable and Hiroshima -- a vegetable, a spinach, three leaves and mulukhiya -- it needs -- a vegetable, ****, sagebrush, a shallot, etc. be mentioned These are vegetables grown and marketed as a food material. moreover, the terrestrial part of the root vegetables which originally are not made into the cultural purpose, i.e., a turnip, -- a leaf, a sweet potato leaf, a potato leaf, a ginseng radix leaf, a Japanese radish leaf, a waste leaf, etc. can be used as a raw material of the vitamin K supply constituent of this invention.

[0008] The deep yellow vegetables used in this invention are botanically formed from the scapus and the deep green leaf. A scapus is a transfer organ which attaches a leaf and a sexual organ, supports a terrestrial part mechanically while aiming at increase of an individual, and attaches a root, and performs the adit of ****** in the meantime. A scapus has fiber which makes a firm cellulose and a firm hemicellulose a subject in the cell of the shape of a rod of the lengthwise direction aiming at mechanical support, i.e., physical external force, at the hyperplasy epidermis and its inside for taking care of an internal organization, and, inside, consists of the vascular bundle for transmitting ****** further. A leaf is an organ which performs photosynthesis, conversion of nutrient matter, evapotranspiration of moisture, etc., and usually consists of the leaf blade section and a leaf pedicel. The leaf blade section consists of the epidermis for protecting a comparatively flexible front face, the mesophyll section containing the chlorophyll which performs photosynthesis and conversion of nutrient matter, and the vein section. The vein section and a leaf pedicel are the organizations for supporting a leaf mechanically like a scapus, and are also performing the work which transmits ******. With the chlorophyll in the above-mentioned mesophyll section, solar energy is used for the carbon dioxide in air, and the moisture sucked up originally, and carbohydrates, such as starch and a saccharide, are compounded. These carbohydrates are disassembled into amino acid and others, it combines with the fertilizer component (mainly nitrogen component) absorbed out of soil, and proteinic composition is performed. In that case, they are collectively compounded by the vitamin K of lipophilicity, vitamin E, beta-carotene, etc., and are stored in the mesophyll section. Conventionally, deep yellow vegetables were only processing of a green leaf and a dry matter, and it was difficult to obtain only the mesophyll section containing many vitamin Ks of lipophilicity, vitamin E, beta-carotene, etc.

[0009] Next, the manufacture approach of the vitamin K supply constituent of this invention is explained in full detail. In this invention, although aimed at the leaf of deep yellow vegetables at least as a processed material, the following down stream processing may be presented from fields, such as cost, including a leaf, a scapus, and the root that stands in a row in a scapus further, without removing a scapus beforehand. The case where a leaf and a scapus are used as a processed material is mentioned as an example, and the following processing processes explain it. In order to make easy softening of the plant tissue by heating first performed at this process, a kitchen knife, a rotary cutter, a guillotine cutter, etc. cut in magnitude of 6-25mm preferably 4-40mm per piece. moreover, natural, in order to remove dust, mud, etc. adhering to a green leaf front face -- it rinses by the stream, the high-pressure jet blast, ultrasonic irradiation, etc. The sequence of a cutting process and a rinsing process may perform whichever first. Then, by centrifugal separation or the gravity flow type, the moisture adhering to the front face of the deep yellow vegetables cut and washed is dehydrated so that attached groundwater may become below 10% weight.

[0010] In this process, in order to perform easily separation with the mesophyll section containing many vitamin Ks, and a leaf pedicel, the vein section and a scapus, boiling water processing for 2 - 7 minutes or direct contact cooking is preferably performed at 85-100 degrees C for 1 - 10 minutes in a 80-120 degrees C (pressurization) temperature requirement, and the mesophyll section is fully softened also in a leaf. that time -- pH of boiling water -- 6.0-8.5 -- it is desirable that it is in the

range of 6.5-8.0 preferably. In direct contact cooking, it is desirable to perform pretreatment preferably immersed in the solution of pH 6.0-8.5 for 30 - 60 minutes for 20 - 120 minutes at the solution of 6.5-8.0. In the above-mentioned softening process, which approach of a batch process and continuous system may be adopted. By this heating, deactivation of the enzyme with a possibility of fading **** chlorophyll coloring matter is carried out in the skillful green of a plant cell not only softening but deep yellow vegetables. That is, also in chlorophyll being decomposed into a FIO phytin and carrying out deactivation of the enzymes, such as yellow, chlorophyllase further faded to blackish brown, and oxidase, from green, heat-treatment is an effective means. By centrifugal separation or the gravity flow type, the moisture which cooled with cold water immediately and adhered to the cut front face of deep yellow vegetables after heating is dehydrated so that the attached groundwater after cooling may become 10 or less % of the weight.

[0011] Then, it is desirable to add the water of the 10 - 100 weight section to the heat-treated deep-yellow-vegetables 100 weight section, and to agitate for 2 - 20 minutes at the temperature of 5-50 degrees C. As for this churning, it is desirable to add the water of 20 - 70 weight section to the above-mentioned deep-yellow-vegetables 100 weight section, and to carry out for 5 - 10 minutes at 10-40 degrees C. By adding water to deep yellow vegetables, the fluidity of the deep yellow vegetables within an agitator is raised, and is unfolded and crushed, and distribution is promoted. The fluidity within an agitator is scarce in the amount of adding water at the time of stirring being under 10 weight sections, and it unfolds, and crushes, and it becomes difficult to promote distribution. Since the fluidity within an agitator increases and crushing fully becomes impossible on the other hand it it adds water more mostly than 100 weight, the dehydration throughput of about [that liquefaction of the mesophyll section becomes difficult] and the back increases, as a result it is disadvantageous in cost. As an agitator used in that case, the agitator of the axis of ordinate for a jam, Anh, confectionery, and bread-making or an axis of abscissa etc. is mentioned. Although the scapus which consists of a firm organization, a leaf pedicel, and the vein section will maintain the original form if an axis of ordinate or the churning shaft of an axis of abscissa is preferably operated at the rotational frequency of 50 - 200rpm 20 to 400 rpm, the mesophyll section softened with heating liquefies. Here, at the rotational frequency of less than 20 rpm, the mesophyll section softened with heating does not fully liquefy, but the amount of acquisition of the mesophyll section obtained according to a solid-liquid-separation process decreases. On the other hand, if it is made to rotate more quickly than 400rpm, a leaf pedicel, the vein section, and a scapus will also be unfolded together, crushing will come to be performed, and it will become difficult to separate the mesophyll section, a leaf pedicel, the vein section, and a scapus according to the following solid-liquid-separation process.

[0012] Although the filter which has a proper mesh as a means which carries out solid liquid separation of a leaf [having stopped the original form] pedicel, the vein section and a scapus, and the mesophyll section that liquefied is used and it is not limited especially, a strainer machine is used suitably. A strainer machine has the churning child who rotates in a cylinder screen, and the leaf pedicel, the vein section and the scapus which stopped the original form, and the mesophyll section can be separated by passing the mesophyll section which liquefied from the cylinder screen tip. Equipping with the mesh of the magnitude of arbitration is possible on the above-mentioned cylinder screen, and the mesh which has the opening which is 0.5-3.0mm is usually used for it. In the filtrate which passed the strainer machine, polyphenol, such as organic acids, such as the mesophyll section organization containing many vitamin Ks of lipophilicity, vitamin E, and beta-carotene, oxalic acid contained in deep yellow vegetables, a tartaric acid, a succinic acid, a glyoxylic acid, and a glycolic acid, and chlorogenic acid, a catechin, tannin, is contained as a water solution. The above-mentioned mesophyll section organization is surrounded by the epidermis containing many organic acids or polyphenol, and consists of a ledged organization and a spongy parenchyma. Chlorophyll is contained in a ledged organization and a spongy parenchyma, and photosynthesis and conversion of nutrient matter are performed. It is an effective means to separate the mesophyll section containing a vitamin K with the water solution containing an organic acid or polyphenol, since the oxalic acid and polyphenol which are contained in deep yellow vegetables through this composition and matter conversion present acridity and an astringent taste, in view of the problem of palatability.

[0013] The various methods of using a centrifugal force and a pressure are employable as separation with the mesophyll section and the above-mentioned water solution which are suspended in the filtrate which passed the strainer machine. For example, it is divided roughly into the separation approach using a centrifugal force by two, centrifugal separation and centrifugal filtration. Generally a centrifugal separator consists of cylinder-like the ball and screw conveyor whose diameter was reduced the diameter of thru/or expanded continuously, the solid particulate which sedimented in the ball outer wall with the centrifugal force is discharged outside the plane with a screw conveyor, and a liquid is overflowed and is discharged outside the plane. The decanter mold centrifugal separator which can separate the solid of the mesophyll section containing a vitamin K and the liquid containing an organic acid or polyphenol as this centrifugal separator is suitable. A centrifugal filter is equipment which separates the solid particulate in the liquid which is hard to separate from a liquid, by rotating the filter wrapped in the filter cloth at high speed, can acquire the centrifugal force of 3000-4000G, and can separate it from the liquid which contains an organic acid and polyphenol by using the mesophyll section containing a vitamin K as a solid.

[0014] The squeezing separation using a pressure is actuation which high pressure is made to act on a liquid and the mixture of a solid particulate, and squeezes a liquid, and there are a batch process and continuous system. In batch process squeezing separation, the strainer machine passage liquid obtained at the last process is put in into a saccate filter cloth, a pressure is applied only from an one direction, a liquid is squeezed, and only a solid particulate remains in a filter cloth. Then, the solid of the mesophyll section containing a vitamin K is recoverable by taking out a solid particulate from a filter cloth. Moreover, in continuous system squeezing separation, it is separable into a liquid and the solid particulate containing a vitamin K by supplying strainer machine passage liquid between the band-like filter cloths of two sheets, twisting around the roll of several, and making a squeezing pressure act. Specifically, a filter press and a belting press can be used. Although the food-grade vitamin K supply constituent manufactured according to the above process has the shape of a paste containing 20 - 50% of moisture and can present practical use in the condition as it is, it is desirable to perform hot-air-drying processing, drum desiccation processing, and freezing vacuum-drying processing according to a conventional method further.

[0015] Furthermore, the case where the leaf and scapus of the dried deep yellow vegetables are used as a processing object is mentioned as an example, and the manufacture approach of the food-grade vitamin K supply constituent of this invention is explained in full detail. In order to dry a plant tissue easily, after cutting, washing and dehydrating like the above-mentioned, it is preferably [air drying by sunlight, and the temperature of 40-80 degrees C] desirable to decrease the moisture of deep yellow

vegetables to 5 – 14 % of the weight preferably three to 18% of the weight by desiccation processing of 50–70–degree C draught drying, the freezing vacuum drying under reduced pressure, etc. In this process which uses the dry matter of a leaf as a processing object, the leaf blade section, scapus, and leaf pedicel from which specific gravity differs as a separation process of a first stage using change arising according to the settling velocity in the inside of the air of the cut dry matter and a consistency difference with air are separated. Since it is disadvantageous in cost to separate a leaf pedicel from the leaf blade section by cutting etc. beforehand at the separation process of a first stage, it is difficult to separate completely the part of the leaf pedicel which stands in a row in the leaf blade section. Therefore, some leaf pedicel mixed in the leaf blade section will be supplied to the separation process of the next second stage. Moreover, some leaf blade section which stands in a row in a scapus is separated together with a scapus at the separation process of a first stage. The mesophyll section which ground the leaf and was finely ground as a separation process of a second stage is classified with the leaf pedicel and the vein section which were ground coarsely. In addition, when using only the dry matter of a leaf as a processing object, the separation process of a first stage is skipped.

[0016] It is desirable to adopt a gravitational field classification as a separation process of a first stage, and this classification can be divided roughly into two, a water plain stream form and a perpendicular style form. In a water plain stream form, while a difference arises in the settling velocity in the inside of air by dropping the mixture of the leaf blade section, a leaf pedicel, and a scapus from raw material input port in a uniform water calm style, a consistency difference with the air in a horizontal direction arises. Since the leaf blade section with small specific gravity falls near an outlet and the large leaf pedicel and large scapus of specific gravity fall near the injection section, both can be classified easily. In a perpendicular style form, it enters from the lower part of the air separator machine which has **** of the JIGUZAKU form where the mixture of the leaf blade section, a leaf pedicel, and a scapus raised cylinder–like **** or classification efficiency after the air current had distributed. A leaf pedicel and a scapus with larger specific gravity than an air separator on–board section exhaust port are discharged for the leaf blade section with small specific gravity from the exhaust port of the air separator machine lower side by the ascending air current outside the plane, respectively, and such mixture can classify both by it.

[0017] The separation process of a second stage separates the mesophyll section with a leaf pedicel and the vein section using a high–speed tumbling mill with for example, grinding / classification capacity. That is, by controlling grinding of a high–speed tumbling mill, and classification conditions, the weak mesophyll section is ground finely systematically, a firm leaf pedicel and the vein section can be ground coarsely systematically, and after classifying these, only the mesophyll section can be obtained by using a screen etc. and dissociating. Drawing 1 is an explanatory view of a high–speed tumbling mill used in grinding and a classification process as an example of this invention. The high–speed tumbling mill shown in drawing 1 consists of the feeding section 1, the grinding section 2, the classification section 3, an air inlet section 4, and the air discharge section 5. It has connected with the periphery section of the grinding section 2, and the tubed feeding section 1 prepared horizontally is equipped with the screw feeder 6 which supplies the leaf dry matter which uses the leaf blade section of deep yellow vegetables as a principal component to the interior to the grinding section 2. The grinding section 2 and the classification section 3 are divided by the reverse conic guide ring 7, the grinding section 2 is arranged at the lower part and the lower part of the guide ring 7 periphery section, and the inside of a guide ring 7 serves as the classification section 3. The grinding section 2 and the classification section 3 are equipped with the first rotary wing 8 and second rotary wing 9 of a rotational frequency adjustable type, respectively. Rotary wings 8 and 9 are driven through the driving mechanism and revolving–speed–control device of a belt, a revolving shaft, etc., respectively by two motors 10 installed in the center section of the body lower part of a mill. Moreover, the air which the air inlet section 4 was established in the body lower part of a mill, and was attracted from the duct of an intake 4 by rotation of the second rotary wing 9 passes along the above–mentioned grinding section 2 and the classification section 3, and is discharged outside the plane from the air discharge section 5 of the shape of a cylinder prepared in the center section of the upper part of a mill body with the mesophyll section pulverized while the leaf organization was classified in the classification section 3.

[0018] In the above–mentioned high–speed tumbling mill, by the gravitational field classification, a scapus and most of leaf pedicels, and the leaf of the separated deep yellow vegetables are supplied in a high–speed tumbling mill from the feeding section, and are ground in the grinding section. The ground leaf rides and goes up from a lower stream of a river to an air current, and in the classification section, fines are discharged outside the plane, and coarse grain is returned to the grinding section of the guide ring lower part by the balance of a centrifugal force and the improvement force of the air current attracted, and is again ground. 3000 to 7500 rpm, preferably, if the rotational frequency of a rotary wing [in / for the rotational frequency of the rotary wing in the grinding section / the classification section] is preferably controlled 700 to 1400 rpm to 4000 – 6000rpm at 800 – 1200rpm, the mesophyll section will be pulverized by 100 micrometers or less, and coarse grinding of the leaf pedicel and the vein section with a firm organization will usually be carried out to the range of 100–1000 micrometers. These coarse–grinding objects are discharged and removed outside the plane after shutdown. This high–speed tumbling mill is called impact type pulverizer, and a hammer mill and a pin mill are used. The particle which a particle 100 micrometers or less consists of about 100% of mesophyll section, and particle size exceeds 100 micrometers, and has it in the range of 1000 micrometers or less consists of about 100% of leaf pedicel, and the vein section, although the mesophyll section is contained slightly. The grinding object discharged high–speed tumbling mill outside the plane is separated into a particle and air from an air exhaust port using the cyclone for dust collectors by the conventional method. Then, if a particle 100 micrometers or less is classified with a sufficient precision using a square shifter and plan shifter, mho gene sensor IZAI, a vibration screen, etc., the mesophyll section containing many vitamin Ks which are fat soluble vitamin, vitamin E, and beta–carotene can be obtained easily.

[0019] A food–grade vitamin K supply constituent can be manufactured by [which carry out back solid liquid separation, or grinds and classifies the dry matter of deep yellow vegetables] having softened the plant tissue of deep yellow vegetables which has the green leaf blade section as mentioned above. Such a food–grade vitamin K supply constituent contains a vitamin K more than 1000microg per 100g. Although a vitamin K has the property which is easy to oxidize, since the alpha–tocopherol (vitamin E) which has the natural antioxidizing effectiveness, and beta–carotene are contained in the constituent obtained by this invention, it does not become a problem at all about the stability of a vitamin K. The food–grade vitamin K supply constituent of this invention can process various food gestalten, such as for example, pans, noodles, confectionary, frozen desert, a wheat flour mix, boiled fish paste, ice cream, and drinks, and can supply a vitamin K easily in the usual eating habits.

[0020] This invention relates to the approach of extracting a vitamin K from said deep yellow vegetables which have the green leaf blade section again using the carbon dioxide in a supercritical condition which liquefied. Although it is not especially limited as deep yellow vegetables of an extract-ed since the vitamin K extract ability of a carbon dioxide is high, that by which the organization of for example, the deep yellow vegetables itself and its leaf was destroyed beforehand is desirable, in view of extraction efficiency. Especially, the solid or dry matter of the mesophyll section with a high vitamin K content separated by the above-mentioned approach is suitable. Drawing 2 is vitamin K extract process drawing of supercritical extraction equipment. the choke damp emitted by Kaisei of a bulb 13, and closing of a bulb 17 from a chemical cylinder 11 in this drawing — the first heat exchanger 14 — cooling — further — a compressor 15 and the second heat exchanger 16 — pressurization — and it warms or cools, adjusts to moderate temperature, and liquefies to the carbon dioxide of a supercritical condition. Subsequently, the liquefaction carbon dioxide which carried out Kaisei of the bulb 17 and was held at the supercritical condition is introduced into the extract tub 18. Under the present circumstances, a bulb 13 is closed, after measuring the amount of carbon dioxides with the balance 12 attached to the chemical cylinder 11 and measuring the specified quantity. The support screens 18a and 18b which arranged the filter paper on the upper and lower sides of the extract tub 18 inside are arranged, and deep yellow vegetables are beforehand thrown into the interior of a tub. The liquefaction carbon dioxide which extracted the vitamin K in the extract tub 18 is introduced into the separation tub 20 by carrying out Kaisei of the bulb 19, and the extract residue which did not pass a filter paper is removed. Then, the inside of the separation tub 20 is decompressed by closing of a bulb 17, and Kaisei of a bulb 21, a carbon dioxide is gasified, and is discharged out of a tub from an exhaust port 22, and a natural vitamin K extract is separated from output port 23.

[0021] the extract approach of this invention which uses the carbon dioxide in a supercritical condition as an extract solvent — for example, the mesophyll section 1 weight section — receiving — a liquefaction carbon dioxide — the 10 - 100 weight section — desirable — 20 - 60 weight section — in addition, it extracts. The extract of a vitamin K is inadequate in the weight ratios of a liquefaction carbon dioxide being under 10 weight sections. Moreover, even if it uses more mostly than the 100 weight sections, the extract effectiveness does not improve so much but the cost of a carbon dioxide increases. Under the present circumstances, they are 20-50 degrees C and the pressure of 100-350kg/cm2 preferably the temperature of 10-60 degrees C. It is 150-300kg/cm2 preferably. If it extracts under conditions, a natural vitamin K can be alternatively extracted from deep yellow vegetables. If it separates from the above-mentioned temperature flow and pressure requirement, since the organic acid and polyphenol which are an acridity component besides green chlorophyll coloring matter will be extracted, it is not desirable. According to above-mentioned extract processing, by decompressing after extract termination, the carbon dioxide which is an extract solvent is gasified and is removed from an extract. Therefore, a great quantity of heat energy or facilities are not needed for separation of an organic solvent like the conventional column chromatography, distillation, and solvent fractionation. And since the chlorophyll coloring matter contained in the mesophyll section does not denaturalize to said harmful matter, a natural vitamin K with high safety can be obtained. The vitamin K obtained by the above-mentioned extract approach can be used as physic, such as prevention of the above-mentioned deficiency disease, and osteogenesis promotion, besides food.

[0022] Measurement of vitamin K concentration has the absorptiometry which measures and carries out the quantum of the absorbance of the absorption-maximum wavelength of a vitamin K, the colorimetric method which is made to react with sodium alcoholate and carries out colorimetry, the gas-chromatography method, a high-performance-chromatography method, etc. In recent years, compared with other analysis methods, it is simple, and the high speed liquid chromatography method with a sufficient quantum precision is widely used as microestimation of a vitamin K. In this invention, if vitamin K analysis is described briefly, it adds to the partially aromatic solvent of ethanol-water (8:2), and the mesophyll section or the vitamin K extract weighed precisely first is ****(ed) for 5 minutes. Next, n-hexane is added and a crude extract is obtained after **** and centrifugal separation. Furthermore, after carrying out [be / it / under / column / which was filled up with silica gel / letting it pass] purification processing, it analyzes by the high-speed liquid chromatograph. Although there are the ultraviolet-rays detecting method and the fluorescence detecting method in a high-speed liquid chromatograph, in order to detect a vitamin K with a sufficient precision, after returning to fluorescence hydroquinone K by the chemical reduction, electric reduction, or platinum black column reduction which used the sodium borohydride, fluorescence detection is carried out and the approach of carrying out a quantum is desirable.

[0023]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these examples at all. In addition, drawing 3 is the flow chart of the manufacture approach of the food-grade vitamin K supply constituent shown in the following examples 1-5.

1kg (g/100g with a vitamin K concentration of 290micro) of Chinese cabbage which is one sort of example 1 deep yellow vegetables was rinsed with the stream, and dust and mud were dropped. The rinsed Chinese cabbage was cut in die length of 20mm using the rotary mold slicer (new sanitary ESA: Product made from EMURA Sale). This was put into 5l. of 98-degree C boiling water, boiling water processing was carried out for 3 minutes, and the leaf was softened. Then, the molten-bath end and cooling with a stream were performed, the ridge by gravity flow was performed, and 1.05kg of softening processing objects of Chinese cabbage was obtained. Subsequently, in the mixer for bread-making (AM-20: Made in the Aicohsha Factory), 250g of water was added to the above-mentioned softening processing object, it agitated for 5 minutes by 80rpm, and the mesophyll section was liquefied. The Chinese cabbage which carried out liquefaction processing was filtered using the strainer machine of 1mm mesh screen wearing, and a leaf pedicel, the vein section, and a scapus were separated with the mesophyll section. Processed the obtained filtrate for 10 minutes with the batch process centrifugal separator of 3000rpm, the solid was made to sediment, and 200g of vitamin K content constituents was obtained from Chinese cabbage. The vitamin K concentration of the obtained constituent was 1,220micro g/100g, and the enrichment factor of a vitamin K was 4.2 times.

[0024] Mulukhiya (g/100g with a vitamin K concentration of 400micro) 1kg which is one sort of example 2 deep yellow vegetables was rinsed with the stream, and dust and mud were dropped. The rinsed mulukhiya was cut in die length of 10mm using the rotary mold slicer (said new sanitary ESA). This was put into 5l. of 90-degree C boiling water, boiling water processing was carried out for 5 minutes, and the leaf was softened. Then, the molten-bath end and cooling with a stream were performed, the ridge by gravity flow was performed, and 1.07kg of softening processing objects of mulukhiya was obtained. Subsequently, in the mixer for bread-making (said AM-20), 200g water was added to the above-mentioned softening processing object, it agitated for

7 minutes by 100rpm, and the mesophyll section was liquefied. The mulukhiya which carried out liquefaction processing was filtered using the strainer machine equipped with 1mm mesh screen, and a leaf pedicel, the vein section, and a scapus were separated with the mesophyll section. Carried out centrifugal separation of the obtained filtrate with the horizontal-type decanter, the solid was made to sediment, and 300g of vitamin K content constituents was obtained from mulukhiya. The vitamin K concentration of the obtained constituent was 1,240micro g/100g, and the enrichment factor of a vitamin K was 3.1 times.
[0025] Parsley (g/100g with a vitamin K concentration of 730micro) 1kg which is one sort of example 3 deep yellow vegetables was rinsed with the stream, and dust and mud were dropped. The rinsed parsley was cut in die length of 10mm using the rotary mold slicer (new sanitary ESA). This was cooked for 5 minutes with 98-degree C heating steam, and the leaf was softened. Then, the molten-bath end and cooling with a stream were performed, the ridge by gravity flow was performed, and 1.05kg of softening processing objects of parsley was obtained. The same processing as an example 1 was performed below, and 250g of vitamin K content constituents was obtained from parsley. The enrichment factor of a vitamin K of the vitamin K concentration of the obtained constituent was 2.3 times in 1,680micro g/100g.
The processing same [1kg (g/100g with a vitamin K concentration of 250micro) of example 4 Japanese-radish leaves] as an example 2 was performed, and 150g of vitamin K content constituents was obtained from the Japanese radish leaf. The enrichment factor of a vitamin K of the vitamin K concentration of the obtained constituent was 4.2 times in 1,050micro g/100g.
[0026] 1kg (g/100g with a vitamin K concentration of 330micro) of Simon 1 No. leaves which are one sort of example 5 sweet potato was rinsed with the ultrasonic washing machine, and dust and mud were dropped. The kitchen knife cut the rinsed Simon leaf in die length of 10mm. This was put into 3l. of 95-degree C boiling water, boiling water processing was carried out for 4 minutes, and the leaf was softened. Then, the molten-bath end and cooling with a stream were performed, the ridge by gravity flow was performed, and 1.05kg of softening processing objects of the Simon leaf was obtained. Subsequently, in the horizontal-type kneader for ** Anh, 1000g of water was added to the above-mentioned softening processing object, it agitated for 4 minutes by 100rpm, and the mesophyll section was liquefied. The Simon leaf which carried out liquefaction processing was filtered using the strainer machine of 2mm mesh screen wearing, and a leaf pedicel, the vein section, and a scapus were separated with the mesophyll section. Processed the obtained filtrate for 10 minutes with the batch process centrifugal separator of 3000rpm, the solid was made to sediment, and 230g of vitamin K content constituents was obtained from the Simon leaf. Furthermore, freezing vacuum-drying processing was performed at 30 degrees C, and the 120g of the above-mentioned constituents from which moisture was removed was obtained. The vitamin K concentration of the obtained constituent was 2,350micro g/100g, and the enrichment factor of a vitamin K was 7.1 times.
[0027] Examples 1-5 are collectively shown in the following table 1.
[Table 1]

実施例	緑黄色野菜	組成比 (%)		ビタミンK*		濃縮率 (%)
		葉部	茎部	生葉	組成物	
1	小松菜	39	61	290	1220	420
2	モロヘイヤ	54	46	400	1240	310
3	パセリ	60	40	730	1680	230
4	大根葉	42	58	250	1050	420
5	シモン葉	40	60	330	2350	710

＊単位：μg 100g

[0028] examples 6-10 — the leaf (g/100g with a vitamin K concentration of 330micro) and 1kg of scapuses which are said Simon 1 No. terrestrial part — a stream — it rinsed by inside and the dust and mud adhering to a front face were removed. After cutting the Simon leaf and stem which were rinsed in die length of 10mm using a rotary system slicer (new sanitary ESA), the ridge by the gravity flow type was performed. Then, it dried for 12 hours with the multistage-type hot air drying equipment set as 70 degrees C, and the 120g Simon terrestrial part dry matter was obtained. At that time, it agitated every 2 - 3 hours, and desiccation was promoted. Subsequently, the leaf and the scapus were separated for the Simon terrestrial part dry matter dried by 8% of moisture using the wind-force sorting machine for a thresh, and the 50g leaf dry matter was obtained. Using the high-speed tumbling mill (ACM pulverizer: Hosokawa Micron CORP.) which shows each obtained leaf dry matter to above-mentioned drawing 1 , adjustable [of the rotational frequency of the rotary wing (8 9) in the grinding section (2) and the classification section (3)] was carried out, and dust was collected for the grinding object discharged outside the plane from the discharge section (5) with the cyclone. Each obtained grinding object let the vibration screen of 100-micrometer mesh made of nylon pass, and obtained the mesophyll section grinding object with a particle size of 100 micrometers or less.
[0029] Examples 6-10 are collectively shown in the following table 2.
[Table 2]

実施例	回転数（rpm）		葉肉部粉砕物（g）	ビタミンK濃度*	
	粉砕部	分級部		生葉	粉砕物
6	4000	1200	37	330	2050
7	5000	1000	38	330	2150
8	6000	800	40	330	1980
9	3000	1500	25	330	850
10	7000	600	27	330	700

*単位：μg／100g

[0030] As shown in Table 2, in the example 9, the rotational frequency of the grinding section was comparatively as small as 3000rpm, and since the grinding effectiveness of a leaf dry matter was not enough, the yield of a mesophyll section grinding object was low. And the rotational frequency of the classification section was greatly written with 1500rpm, a part of leaf pedicel other than the mesophyll section and vein section mixed, and vitamin K concentration was also low. Moreover, in the example 10, since the rotational frequency of the classification section was as small as 600rpm, the yield of a mesophyll section grinding object was low. And the rotational frequency of the grinding section was written comparatively greatly with 7000rpm, a part of leaf pedicel and vein section were ground by the particle size of 100 micrometers or less, and vitamin K concentration was also low. the rotational frequency of the first rotary wing [in / on the other hand / the grinding section] — the range of 4000 – 6000rpm — and in the examples 6-8 which controlled the rotational frequency of the second rotary wing in the classification section in the range of 800 – 1200rpm, the result with good yield and its vitamin K concentration of a mesophyll section grinding object was obtained. Thus, by controlling the engine speed of the rotary wing in the grinding section and the classification section in the above-mentioned range shows that the yield and its vitamin K concentration of the mesophyll section improve.
[0031] Extract processing of the mesophyll section grinding object obtained in the example 7 was carried out using the supercritical extraction equipment shown in drawing 2 of the example 11 above-mentioned, and the vitamin K was obtained. That is, 1kg of mesophyll section grinding objects was put into the extract tub (18), and temperature control and the liquefaction carbon dioxide which pressurized and reached the supercritical condition were introduced into the extract tub (18) for the carbon dioxide emitted from the chemical cylinder (11) with the heat exchanger (14 16) and the compressor (15). They are the temperature of 40 degrees C, and the pressure of 250kg/cm2, using the liquefaction carbon dioxide in this supercritical condition as an extract solvent. Extract processing of the above-mentioned grinding object was carried out under conditions. The support screen (18a, 18b) of 50 micrometers of openings has been arranged, and the filter paper (Watt Mann filter paper: grade 2) of No2 is arranged on the upper and lower sides of an extract tub (18) at the inside. The carbon dioxide of vitamin K content was introduced into the separation tub (20) after extract processing, and the extract residue on the above-mentioned filter paper was removed. Then, it is a pressure in a separation tub (20) 50kg/cm2 Decompressed, the carbon dioxide was made to gasify and 11.6g of natural vitamin K extracts was obtained. The vitamin K concentration in the obtained extract was 250,000micro g/100g.
[0032]
[Effect of the Invention] According to the manufacture approach of the vitamin K supply constituent of this invention, the vitamin K contained in the mesophyll section in deep yellow vegetables can be obtained by the comparatively easy processing approach. Since the obtained vitamin K constituent is using as the raw material the deep yellow vegetables currently taken in for years with the usual eating habits, palatability is good and does not pose a problem at all on insurance. The matter harmful in the vitamin K obtained seems moreover, according to the extract approach of the vitamin K of this invention, not to remain, in order to use a carbon dioxide as an extract solvent.

[Translation done.]

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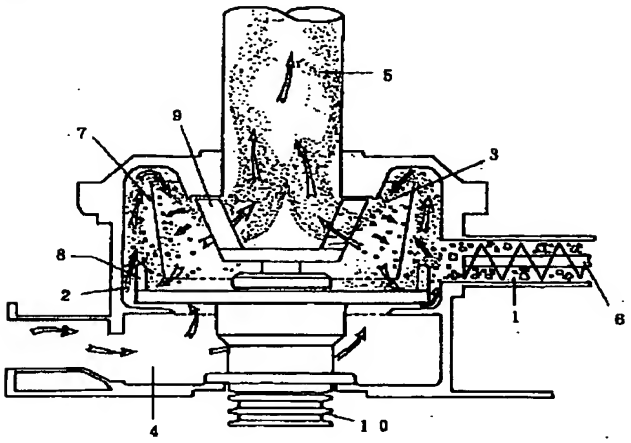
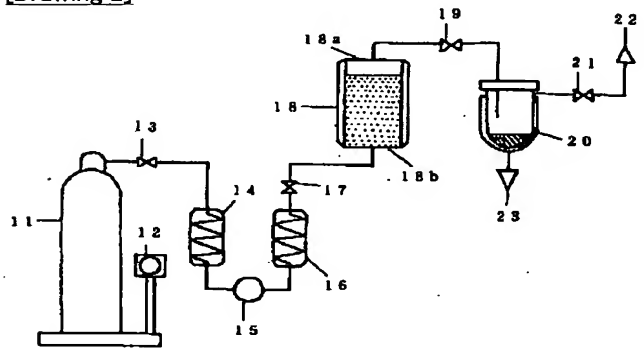
DRAWINGS

[Drawing 1]



[Drawing 2]



[Drawing 3]